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(54) Title: THERMOSTABLE AND BIOLOGICALLY SOLUBLE MINERAL FIBRE COMPOSITIONS

(57) Abstract

A fiberisable mineral composition which is thermostable and has a high dissolution rate in biological fluids and which consists essentially of 56 - 65 w/w % of SiO_2, ≤ 5 w/w % of Al_2O_3, 10 w/w % of CaO, 23 - 36 w/w % of MgO, and Sm(F) 8 w/w %, of FeO + Fe_2O_3, the total amount of FeO and Fe_2O_3 calculated as FeO. A mineral fibre material made from the composition and used for thermal and/or acoustic insulation purposes or as a plant growing medium or substrate.

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THERMOSTABLE AND BIOLOGICALLY SOLUBLE MINERAL FIBRE COMPOSITIONS

The present invention relates to thermostable mineral compositions and more specifically relates to thermostable mineral compositions being soluble in biological fluids. Even more specifically the present invention relates to mineral fibres formed from the mineral compositions and relates to mineral fibre insulation and a mineral fibre plant growing medium made from these compositions.

Mineral fibre insulation is widely used and has been a commercial product for a long period of time. The insulation products are made from mineral raw materials such as rock or slag which are melted and spun into fibres which a binder holds together. The binder is usually a phenol-formaldehyde resin or a urea-modified phenol-formaldehyde resin.

It is well known that mineral fibre insulation products are advantageous as compared to glass fibre insulations products in their higher fire resistance, i.e. an excellent thermostability. Typically, glass wool withstands temperatures up to around 650°C whereas mineral wool is capable of withstanding temperatures up to 1000°C. It is highly desirable to maintain or even increase this excellent property in any modification of the hitherto known mineral fibre products.

Recently, more attention has been put to health issues in connection with various fibrous material, including insulation wool fibres. It is well known that inhalation of certain types of fibres such as asbestos fibres may lead to respiratory diseases, including lung cancer. It is believed that an important factor is the ability of the asbestos fibres to remain in the lung for extended periods of time. Although there has not yet been provided any evidence of manmade fibre being the cause of respiratory or other diseases in man, it is desirable to provide mineral fibres with an increased dissolution rate in biological fluids, since it is expected that such fibres will have a considerably shorter half-time in the lung upon inhalation.

WO 89/12032 discloses inorganic mineral fibre compositions among

which some have passed the ASTM E-119 two hour fire test as well as exhibit low durabilities in physiological saline solutions, i.e. have high dissolutions rates therein. The components of the disclosed compositions may vary considerably. However, all the disclosed compositions are made from pure metal oxides or from less pure raw materials with addition of pure oxides which make the disclosed compositions very costly.

The object of the present invention is to provide a fiberisable mineral composition made from naturally occurring and inexpensive raw materials which has a high dissolution rate in biological fluids and exhibits an excellent thermostability.

The present invention provides a fiberisable mineral composition which is thermostable and has a high dissolution rate in biological fluids and which consists essentially of

SiO_2	56 - 65 w/w%
Al_2O_3	≤ 5 w/w%
CaO	≤ 10 w/w%
MgO	23 - 36 w/w%
FeO + Fe_2O_3	≤ 8 w/w%,

the total amount of FeO and Fe_2O_3 calculated as FeO.

Surprisingly it has been found that mineral fibres having both a high dissolution rate in biological fluids and an excellent thermostability can be formed from mineral compositions of naturally occurring raw materials such as olivine, quartz, dolomite and iron ore.

The compositions of the invention may e.g. be prepared from the following naturally occurring raw materials:

Olivine sand	about 66 %
Quartz sand	about 34 %.

According to the present invention, a preferred range for the total amount of CaO, MgO, FeO and Fe_2O_3 in the mineral composition of the

invention is:

$$35 \text{ w/w\%} \leq CaO + MgO + FeO + Fe_2O_3 \leq 40 \text{ w/w\%}.$$

A preferred range for the total amount of CaO, FeO and Fe_2O_3 in the mineral composition of the invention is:

$$CaO + FeO + Fe_2O_3 \leq 15 \text{ w/w\%}.$$

The mineral composition of the present invention is particularly suitable for the manufacture of mineral fibres by the method disclosed e.g. in WO 92/06047.

For the manufacturing of fine fibres e.g. by this method a composition having a viscosity of approximately 15 poise at the working temperature is necessary. On the other hand it is also desirable that the melt composition has a viscosity not lower than approximately 4 poise at the working temperature.

It is not obvious that the rate of dissolution of the mineral fibre composition can be increased while maintaining other necessary properties. As mentioned above, the melt viscosity must be maintained within a narrow range in order to allow fiberisation by the manufacturing methods currently in use. The resulting mineral wool must be sufficiently durable to maintain its physical integrity throughout the life-time of the building, ship or other location of final use. Furthermore, the resulting mineral wool must be sufficiently thermostable to provide excellent fire resistance to the final insulation product.

The viscosity of a mineral melt composition is dependent on the total content of silica and alumina: high total silica and alumina results in a high viscosity and vice versa. Accordingly, the viscosity provides certain restrictions on how the composition can be modified.

It is believed that the amount of magnesia and ferrous/ferric oxide components in a mineral composition has a significant influence on the thermostability of the mineral fibre. The ferrous/ferric oxide

plays the important role of a crystal nucleating agent in the conversion of the mineral fibre material from an amorphous condition to a crystalline or pseudo crystalline state during external influence of heat, i.e. during heat-up or fire. Accordingly, this provides certain restrictions on the minimum amount of ferrous/ferric oxide component present in the composition. It should be noted that mineral fibre material without ferrous or ferric oxide may be capable of withstanding high temperatures which are reached by slow heat-up in contrast to the fast heat-up resulting e.g. from external fire. As mentioned above, when mineral fibre material is subjected to fire (sudden and/or fast heat-up), the structure of the material, i.e. the mineral wool, is converted from an amorphous condition to a crystalline state and, accordingly, the thermostability of the mineral fibre material requires the presence of a crystal nucleating agent in the fibre material. On the other hand it is expected, e.g. from WO 89/12032, that the presence of alumina and ferrous/ferric oxide components in the mineral composition has a significant negative influence on the rate of dissolution, cf. below.

The rate of dissolution or durability, however, provides the most complicated restriction. The mineral wool must be relatively inert to moisture attack at the installation site, but it must dissolve quickly in the lung. Since both these situations involve water attack on the fibres under nearneutral acid-base conditions, it is also surprising that this requirement can be met by compositional modifications.

In the present specification and claims, the term "biological fluid" denotes physiological salt or saline solutions as well as any fluid present in vivo in mammals.

Another advantageous fiberisable mineral composition of the invention consists essentially of:

SiO_2	60 - 65 w/w%
Al_2O_3	≤ 4 w/w%
CaO	≤ 10 w/w%
MgO	23 - 36 w/w%

$FeO + Fe_2O_3$	2 - 8 w/w%,

the total amount of FeO and Fe_2O_3 calculated as FeO.

The present invention also relates to mineral fibre material made from a mineral composition according to the invention.

In a preferred embodiment of the invention, mineral fibre material according to the invention preferably has a sintering temperature of at least 1000°C, more preferably at least 1100°C, especially at least 1200°C.

The invention further relates to a method of increasing the rate of dissolution in a biological fluid of a thermostable mineral fibre material, in which method a composition according to the invention is used for preparing the mineral fibre material.

The mineral fibre material according to the invention which is thermostable and has a high dissolution rate in biological fluids is useful for thermal and/or acoustic insulation purposes or as a plant growing medium or substrate.

Another advantageous fiberisable mineral composition of the invention consists essentially of:

SiO_2	60 - 65 w/w%
Al_2O_3	0.5 - 3 w/w%
CaO	≤ 8 w/w%
MgO	23 - 36 w/w%
$FeO + Fe_2O_3$	2 - 8 w/w%,

the total amount of FeO and Fe_2O_3 calculated as FeO.

Yet another advantageous fiberisable mineral composition of the invention consists essentially of:

SiO_2	59 - 65 w/w%
Al_2O_3	≤ 2 w/w%
CaO	≤ 8 w/w%

MgO	23 - 36 w/w%
FeO + Fe_2O_3	1 - 8 w/w%,

the total amount of FeO and Fe_2O_3 calculated as FeO.

EXAMPLE

The dissolution rate and the thermostability of mineral fibres made from known compositions or comparison compositions and a composition of the invention, respectively, was determined as described below. The fibres were made by melting the mineral composition to be tested in a conventional furnace, followed by spinning the fibre material into mineral wool. Binder was not applied.

The following mineral fibre compositions were tested:

Composition A:	Commercial mineral fibre composition manufactured by Rockwool Lapinus B.V., Roermond, Netherlands.
Composition B, C, D:	Comparison mineral fibre compositions.
Composition E, F:	Mineral fibre compositions according to the invention.

The constituents of each test composition is shown in Table 1. It is to be understood that in addition to the constituents mentioned in Table 1 each of the tested fibre compositions contained up to a total of 2 w/w% of other constituents (traces) forming part of the raw materials used. Such other constituents may include, for example, manganous oxide, chromium oxide and various sulfur compounds. However, the percentages in Table 1 are standardised to a total of 100 w/w% of the listed constituents.

TEST METHODS

Dimensions of the Fibre Samples

The samples were sieved, and the fraction below 63 μm was used for

the tests.

For each sample, the fibre diameter distribution was determined, measuring the diameter and length of 200 individual fibres by means of an optical microscope (1000 X magnification). The readings were used for calculating the specific surface of the fibre samples, taking into account the density of the fibres.

Measurements of Rate of Dissolution (Stationary Set-Up)

300 mg of fibres were placed in polyethylene bottles containing 500 ml of a modified Gamble's solution (i.e. with complexing agents) at pH 7.5. Once a day the pH was checked and if necessary adjusted by means of HCl.

The tests were carried out during a one week period. The bottles were kept in water bath at 37 °C and shaken vigorously twice a day. Aliquots of the solution were taken out after one and four days and analysed for Si on an Perkin-Elmer Atomic Absorption Spectrophotometer.

The modified Gamble's solution, adjusted to pH 7.5 ± 0.2, had the following composition:

	g/l
$MgCl_2 \cdot 6H_2O$	0.212
NaCl	7.120
$CaCl_2 \cdot 2H_2O$	0.029
Na_2SO_4	0.079
Na_2HPO_4	0.148
$NaHCO_3$	1.950
(Na2-tartrate)$\cdot 2H_2O$	0.180
(Na3-citrate)$\cdot 2H_2O$	0.152
90% Lactic acid	0.156
Glycine	0.118
Na-pyruvate	0.172
Formalin	1 ml

Calculations

Based on the dissolution of SiO_2 (network dissolution), the specific thickness dissolved was calculated and the rate of dissolution established (nm/day). The calculations are based on the SiO_2 content in the fibres, the specific surface and the dissolved amount of Si.

Thermostability

The thermostability expressed as the sintering temperature of the fibre compositions A-F was established by the following method:

A sample (5 x 5 x 7.5 cm) of mineral wool made of the fibre composition to be tested was placed in a furnace pre-heated to 700°C. After 0.5 hours exposure the shrinkage and the sintering of the sample were evaluated. The method was repeated each time with a fresh sample and a furnace temperature 50°C above the previous furnace temperature until the maximum furnace temperature, at which no sintering or no excessive shrinkage of the sample was observed, was determined.

The test results are shown in Table 2 below.

TABLE 1

Components in w/w%

	Prior art compositions				Inventive compositions	
	A	B	C	D	E	F
SiO_2	46.8	50.8	58.6	61.3	62.0	64.6
Al_2O_3	13.2	0.8	3.7	0.8	0.6	0.8
TiO_2	2.9	0.1	0.5	0.2	0.1	0.3
FeO	6.3	0.1	6.0	4.1	7.1	1.9
CaO	17.2	31.0	23.6	12.8	6.1	0.3

MgO	9.6	17.0	6.8	20.3	23.7	31.6
Na2O	2.8	0.1	0.2	0.1	0.1	0.2
K2O	1.2	0.1	0.6	0.4	0.3	0.3

TABLE 2

Composition	A	B	C	D	E	F
Sintering temp. (°C)	1050	750	750	800	1200	1150
Dissolution* pH = 7.5	3	45	6	32	32	45

*: Dissolution rate of Si (nm/day), 1st-4th day.

The test results clearly demonstrate that the fibres formed from the composition of the invention have an excellent thermostability - expressed as a sintering temperature of 1150°C and 1200°C, respectively - in comparison with the prior art fibres. The commercial product (composition A) exhibits also a high thermostability whereas the comparison compositions B, C and D exhibit relatively poor thermostabilities.

The comparative composition B has a higher dissolution rate than the comparative compositions A and C. These results are not surprising, since the total amount of alumina and ferrous/ferric oxide in composition B is less than 1 w/w%. The sintering temperature, however, is unacceptably low.

By comparing the comparative compositions B, C and the comparative composition D it is seen that it is possible to obtain an increased sintering temperature by decreasing the content of CaO even with a relative low content of FeO.

For the inventive compositions E and F an excellent thermostability is obtained as compared to e.g. the comparative compositions C and D by decreasing the content of CaO and increasing the content of MgO.

From the results it is concluded that the mineral fibres made from the compositions of the invention have excellent thermostabilities as well as high dissolution rates in biological fluids.

CLAIMS

1. A fiberisable mineral composition which is thermostable and has a high dissolution rate in biological fluids and which consists essentially of

SiO_2	56 - 65 w/w%
Al_2O_3	≤ 5 w/w%
CaO	≤ 10 w/w%
MgO	23 - 36 w/w%
$FeO + Fe_2O_3$	≤ 8 w/w%,

the total amount of FeO and Fe_2O_3 calculated as FeO.

2. A mineral composition according to claim 1 which consists essentially of

SiO_2	59 - 65 w/w%
Al_2O_3	≤ 2 w/w%
CaO	≤ 8 w/w%
MgO	23 - 36 w/w%
$FeO + Fe_2O_3$	1 - 8 w/w%,

the total amount of FeO and Fe_2O_3 calculated as FeO.

3. A mineral composition according to claim 1 or 2, wherein the total amount of CaO, MgO and $FeO + Fe_2O_3$ is:

$$35 \text{ w/w\%} \leq CaO + MgO + FeO + Fe_2O_3 \leq 40 \text{ w/w\%}.$$

4. A mineral composition according to any of the claims 1-3, wherein the total amount of CaO and $FeO + Fe_2O_3$ is:

$$CaO + FeO + Fe_2O_3 \leq 15 \text{ w/w\%}.$$

5. A mineral fibre material which is thermostable, and has a high dissolution rate in biological fluids, and is made from a mineral composition according to any of the claims 1-4.

6. A mineral fibre material according to claim 5 which preferably has a sintering temperature of at least 1000°C, more preferably at least 1100°C, especially at least 1200°C.

7. A method of increasing the dissolution rate in a biological fluid of a thermostable mineral fibre material, wherein a composition according to any of the claims 1-4 is used for preparing the mineral fibre material.

8. Use of a mineral fibre material according to claim 5 or 6 for thermal and/or acoustic insulation purposes.

9. Use of a mineral fibre material according to claim 5 or 6 as a plant growing medium or substrate.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/DK 93/00437

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: C03C 13/06, C03C 3/087, A01G 31/00
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: C03C, C05G, A01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, A1, 0459897 (ISOVER SAINT-GOBAIN), 4 December 1991 (04.12.91), abstract --	1-8
A	WO, A1, 8705007 (MANVILLE CORPORATION), 27 August 1987 (27.08.87), abstract --	1-8
A	WO, A1, 9209536 (PAROC OY AB), 11 June 1992 (11.06.92), abstract --	1-8
A	EP, A1, 0201426 (ISOVER SAINT-GOBAIN), 17 December 1986 (17.12.86), abstract --	9

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"&" document member of the same patent family

Date of the actual completion f the international search	Date of mailing of the international search report
16 May 1994	06 -06- 1994
Nam and mailing address f the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM	Authorized officer May Hallne

INTERNATIONAL SEARCH REPORT

International application No.
PCT/DK 93/00437

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searches without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☒ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

16/04/94

International application No.
PCT/DK 93/00437

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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